

Communication

**Lewis Acid Enhancement of Proton Induced CO Cleavage:
Bond Weakening and Ligand Residence Time Effects**

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Lewis Acid Enhancement of Proton Induced CO₂ Cleavage: Bond Weakening and Ligand Residence Time Effects

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Supporting Information Placeholder

ABSTRACT: Though Lewis acids (LAs) have been shown to have profound effects on carbon dioxide (CO₂) reduction catalysis, the underlying cause of the improved reactivity remains unclear. Herein, we report a well-defined molecular system for probing the role of LA additives in the reduction of CO₂ to carbon monoxide (CO) and water. Mo(0) CO₂ complex (**2**) forms adducts with a series of LAs, demonstrating CO₂ activation that correlates linearly with the strength of the LA. Protons induce C–O cleavage of these LA adducts, in contrast to the CO₂ displacement primarily observed in the absence of LA. CO₂ cleavage shows dependence on both bond activation and the residence time of the bound small molecule, demonstrating the influence of both kinetic and thermodynamic factors on promoting productive CO₂ reduction chemistry.

As the terminal product of fossil fuel combustion, the conversion of carbon dioxide (CO₂) to energy-dense, liquid fuels is a necessary step in closing an anthropogenic carbon cycle.¹ Technologies for the capture,² copolymerization,³ and hydrogenation⁴ of CO₂ have recently emerged, and their study and design is topical. However, the controlled reduction of CO₂ with protons and electrons is most relevant to artificial photosynthesis and couples most directly to the storage of renewable energy in chemical bonds.^{1,4,5} Due to the kinetic stability of CO₂,⁶ the range of products formed in a narrow potential window, and competing reduction reactions,^{5b,8}

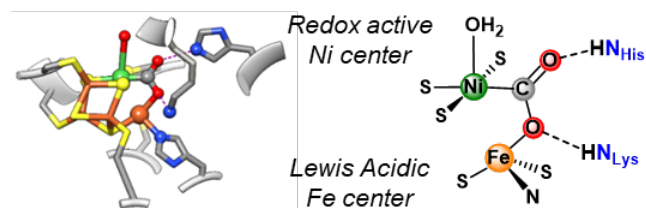


Figure 1. Solid-state structure (left, PDB: 4UDX)⁷ and schematic representation (right) of the CO₂-bound NiFe-CODH active site.

efficient and robust catalysts capable of the selective reduction of CO₂ remain a subject of significant interest.^{6a}

In nature, the two-electron two-proton reduction of CO₂ is executed reversibly by CO-Dehydrogenases (CODH).⁹ The enzyme active site of NiFe CODH features a redox active Ni center and an Fe(III) ion that coordinate CO₂ in a μ - η C: η O binding motif (Figure 1).^{9b} Added Lewis acids (LAs) promote rate enhancements and redox potential shifts in electrocatalytic CO₂ reduction.¹⁰ This strategy of cooperative CO₂ activation has inspired molecular mimics in the form of ligand scaffolds that feature LAs in the coordination sphere,¹¹ heterobimetallic complexes,¹² exogenous LA addition to CO₂ bound metal complexes or CO₂ reduction intermediates,^{9a,13} and reduction catalysis combining transition metals and diboranes.¹⁴ Though LAs are capable of promoting CO₂ binding^{9a} and increasing the degree of CO₂ activation,^{13c} systematic investigations of their effect on reactivity of the bound CO₂ unit remain scant. Herein, we describe a study correlating Lewis acidity and the degree of CO₂ activation in a low-valent Mo complex.¹⁵ Moreover, we demonstrate that LA addition facilitates C–O bond cleavage, chemistry that does not proceed from the parent LA-free CO₂ complex, via *both* kinetic stabilization and increased small molecule activation.

Dinitrogen adduct **1** reversibly binds CO₂, resulting in formation of an η^2 -CO₂ complex, **2** (Scheme 1). Under an atmosphere of ¹³CO₂, the ³¹P{¹H} and ¹³C{¹H} NMR spectra display a coupling doublet and triplet at 62.8 and 192.4 ppm (²J(C,P) = 29.3 Hz), respectively, consistent with coordination of a single ¹³CO₂ molecule.¹⁶ The IR spectrum of **2** displays stretches at 1716 and 1198 cm⁻¹, sensitive to ¹²C/¹³C isotopic labeling, again supporting a bound CO₂ motif.¹⁶⁻¹⁷ Solid-state analysis of single crystals of **2** grown under a CO₂ atmosphere confirm the η^2 binding mode (Figure 2).

Interested in the thermodynamics of this reversible small molecule binding, longitudinal relaxation (T₁) times were measured for the relevant ¹³C and ¹⁵N resonances of an equilibrium mixture of **1**-¹⁵N, **2**-¹³C, ¹⁵N₂ and ¹³CO₂. Uncharacteristically short values

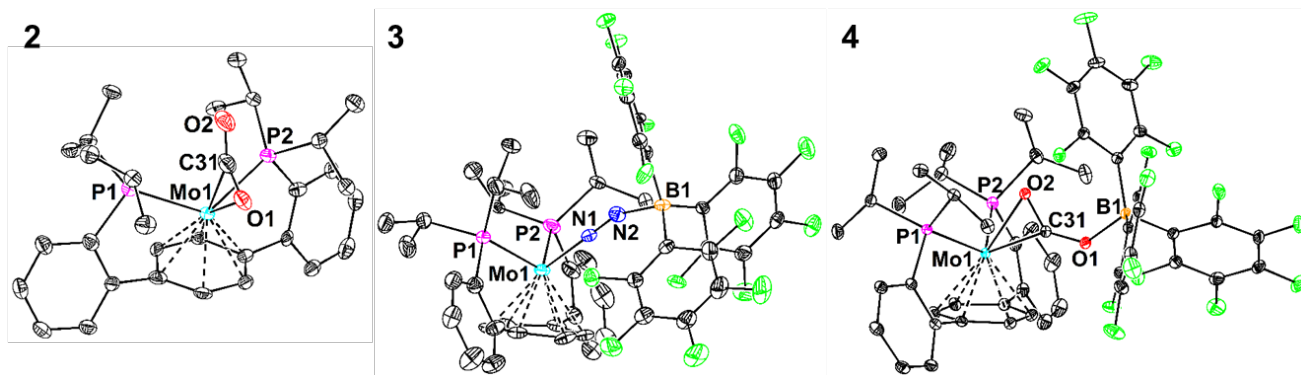
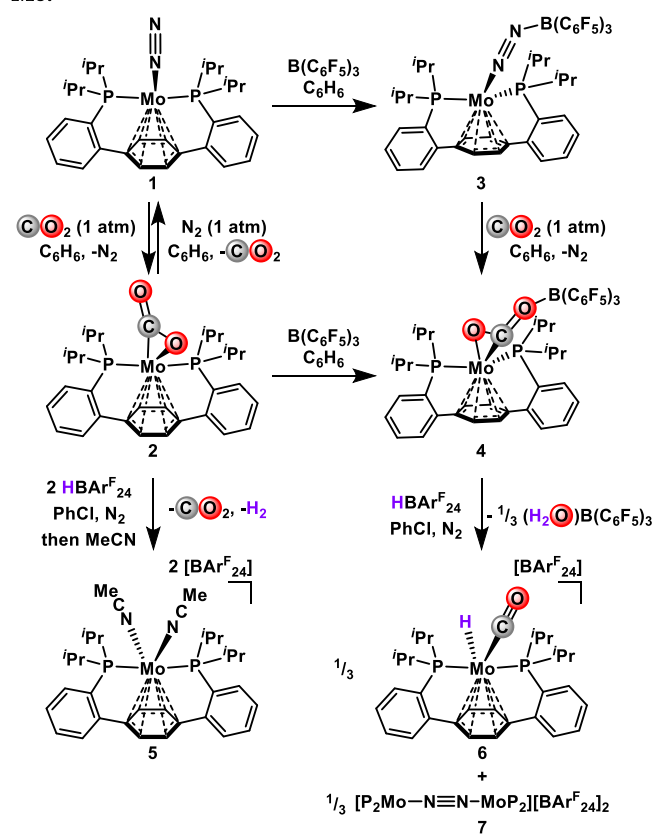


Figure 2. Solid-state structures of complexes **2-4**. Thermal anisotropic displacement ellipsoids are shown at the 50% probability level. H-atoms are omitted for clarity. Selected bond distances [Å] and angles [°]—**3**: Mo1–N1 1.913(2), N1–N2 1.163(3), N2–B1 1.585(37), \angle Mo1–N1–N2 179.1(3), \angle N1–N2–B1 158.2(1.2); **4**: Mo1–O2 2.2535(6), Mo1–C31 2.0574(8), O2–C31 1.246(1), C31–O1 1.275(1), O1–B1 1.554(1), \angle O2–C31–O1 130.93(8), \angle C31–O1–B1 132.13(7).

Scheme 1. CO₂ binding and LA adduct formation at low-valent Mo.⁺



^tHBAr^F₂₄ = [H(Et₂O)₂][BAR^F₂₄] (BAR^F₂₄ = tetrakis[3,5-bis(trifluoromethyl)phenyl]borate)

were observed for **1**-¹⁵N, free ¹⁵N₂, **2**-¹³C, and free ¹³CO₂—5.1(4), 4.9(3), 12.5(4), and 16.8(7) s, respectively.¹⁸ These short and near equivalent T₁ times suggest an exchange process that enables new relaxation pathways unavailable to the free small molecules.¹⁹ In the case of CO₂, exchange was confirmed by magnetization transfer. The high lability of the CO₂ ligand was reflected in the reactivity of **2**. Addition of excess acid to **2** at room temperature resulted in CO₂ dissociation and formation of Mo(II) dication **5** (Scheme 1), via a Mo hydride cation,²⁰ which has been observed in stoichiometric reactions with acid. In CO₂ reduction electrocatalysis, conversion to the metal hydride moves selectivity away from CO, affording either formate or H₂, and representing a branching point in terms of defining the selectivity of CO₂ reduction.²¹

Despite its implication as a critical step in CO₂ to CO reduction catalysis,²² there is a paucity of reports of the protonation of well-defined CO₂ adducts of transition metals.^{13a,23} Indeed, protolytic dissociation and subsequent gas analysis was a common characterization technique for metal-CO₂ complexes.²⁴

Borane LAs have been employed to activate metal coordinated small molecules.^{13a,13c,25} Addition of the strong LA tris(pentafluorophenyl)borane (B(C₆F₅)₃) to complex **1** affords the LA/base adduct **3** (Scheme 1), as confirmed by XRD (Figure 2). The bond metrics of complex **3** are consistent with significant activation of the N₂ unit.²⁶ The solid-state IR spectrum corroborates weakening of the N–N bond, with the stretch red shifting by 134 cm^{−1}. NMR spectroscopy supports a strong borane/nitrogen interaction in solution, with both the ¹⁹F (−135.0, −157.9, and −166.8 ppm)²⁷ and ¹¹B (−14.4 ppm)²⁸ spectra consistent with four-coordinate boron.

Treating **3** with CO₂, or **2** with B(C₆F₅)₃, results in the formation of a new LA adduct, **4**, quantitatively. Contrasting the equilibrium between complexes **1** and **2**, which slightly favors N₂ binding (K_{eq} = 0.48), addition of B(C₆F₅)₃ renders CO₂ binding irreversible (Scheme 1), likely a consequence of the strong B–O interaction; **4** is stable under N₂ in both the solid-state and solution. The triplet for the ¹³CO₂ unit of isotopically labeled **4**-¹³C moves downfield relative to **2** (218.9 ppm, C₆D₆) and exhibits smaller ²J(C,P) scalar coupling (11.47 Hz). Akin to **3**, the ¹¹B and ¹⁹F NMR data are consistent with four-coordinate boron.

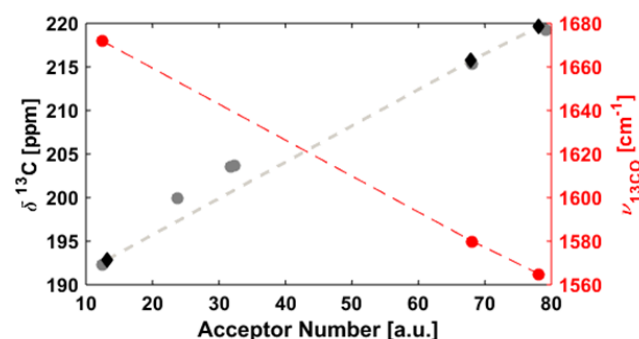
The solid-state structure of **4** exhibits a μ-η²C,O:ηO bridging CO₂ unit between Mo and B (Figure 2). Borane binding to metal-coordinated CO₂ is rare,^{13c} but **4** displays similar bond metrics to such complexes. The structural parameters are consistent with significant CO₂ activation, a phenomenon also borne out in the IR spectrum. The stretches for the CO₂ unit shift to 1602 cm^{−1} and 1218 cm^{−1}, as confirmed by isotopic labeling.

When stabilized with a LA, the reactivity of the Mo CO₂ complexes is decidedly different. The reaction of **4**-¹³C with HBAr^F₂₄ results in the formation of a single diamagnetic Mo complex (Scheme 1). The ³¹P{¹H} and ¹³C{¹H} NMR spectra display a doublet (92.64 ppm) and triplet (220.08 ppm), respectively (²J(P,C) = 14.6 Hz), consistent with CO₂ cleavage to a metal-bound carbonyl. The identity of this product was confirmed as carbonyl hydride cation, **6**-¹³C, via XRD and independent synthesis.²⁹

A balanced reaction for the formation of **6** requires a reductant. When run under N₂, the electrons are provided by **1**, which is generated under the reaction conditions upon borane displacement. Concomitantly with generation of **6**, a paramagnetic Mo(I)–N₂–Mo(I) dinuclear complex,

7, is formed, as confirmed by XRD. Quantifying conversion to **6** shows *ca.* 33% C–O cleavage, consistent with a process involving **1** acting as a single electron reductant; one electron oxidation of **1** with [Fc][BARF₂₄] likewise provides **7**. Borane speciation in the protonation reactions was tracked by ¹⁹F NMR spectroscopy, supporting formation of a bis(borane) hydroxide³⁰ and subsequent protonation to a borane aquo adduct.³¹ Remarkably, LA coordination “turns on” C–O cleavage chemistry, affording CO and H₂O from CO₂ and acid. Borane binding facilitates the delocalization of electron density from the low-valent Mo center into the LUMO of CO₂, in a push-pull mechanism, similar to the “bifunctional attack” proposed for NiFe-CODH.⁷

Figure 3. CO₂ Activation as a function of Lewis Acidity.*



*The ¹³C chemical shift of the CO₂ ligand, in PhCl (♦) and PhCl/Et₂O (●), tracks inversely with the C–O stretching frequency (●).

Interested in the generality of the CO₂ activation observed upon LA coordination to **2**, a series of alkali metal (Na(BARF₂₄) and Cs(BARF₂₄)) and borane (B(C₆H₂F₃)₃, B(C₆F₅)₃, and B(C₆H₃(CF₃)₂)₃) LAs were added to **2**-¹³C. In each case, ¹³C{¹H} and ³¹P{¹H} NMR spectroscopies supported adduct formation, displaying resonances shifted downfield and upfield, respectively, from those of **2** (Tables 1 and S2). The degree of CO₂ activation, as reported by the ¹³C chemical shift, trends linearly with the strength of the LA, as quantified by the acceptor number (AN, Figure 3).³² A similar linear trend is seen when comparing AN vs. ν_{CO₂},³³ suggesting that, in this case, the ¹³C chemical shift of the bound CO₂ ligand correlates with the degree of C–O bond activation.

Revisiting protonation with these new LA adducts (Scheme 2),³⁴ we were gratified to see that in all cases, C–O bond cleavage was enhanced (Table 1). The extent of C–O cleavage³⁵ in PhCl/Et₂O³⁶ increased to roughly the same level, in the range of 4–9%, and not proportionally with the LA AN. Changing to neat PhCl resulted in a further increase to bond cleavage up to 13–16%. Importantly, a two-fold increase in formation of **6**-¹³C is observed for B(C₆H₂F₃)₃ and B(C₆F₅)₃ adducts of **2**-¹³C, despite little perturbation in their respective ¹³C NMR chemical shifts between the two solvent systems. These data are inconsistent

Scheme 2. Protonation of *in situ* formed LA adducts.

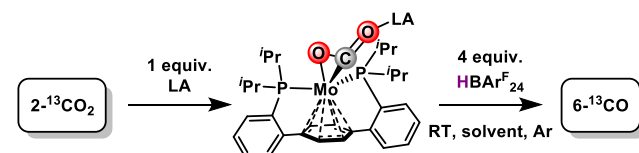


Table 1: CO₂ Activation, Exchange Rate, and Cleavage Data

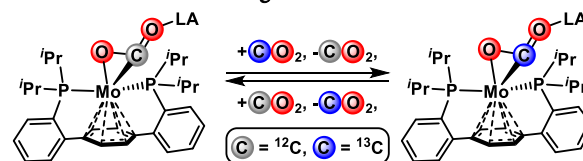
	LA	AN	δ ¹³ C (ppm)	Rate x 10 ⁻⁶ (s ⁻¹)	% CO Cleavage	
					Abs ^a	Rel ^b
PhCl/Et ₂ O	None	12.4	192.3	>200 ^c	0	0
	Cs(BARF ₂₄)	23.7	199.9	20	7	21
	Na(BARF ₂₄)	31.8	203.5	6	4	12
	Na(BARF ₂₄) ^d	32.4	203.7	2	5	15
	B(C ₆ H ₂ F ₃) ₃	68.1	215.3	5	4	12
	B(C ₆ F ₅) ₃	79.2	219.3	9	9	18
PhCl	None	13.2	192.9	>200 ^c >70 ^e	1 10 ^f	3 30 ^f
	B(C ₆ H ₂ F ₃) ₃	67.9	215.7	2	13	39
	B(C ₆ F ₅) ₃	78.1	219.6	2	17 33 ^g	51 99 ^g
	B(C ₆ H ₃ (CF ₃) ₂) ₃	82.7	219.1	1	16	48

^aDetermined by relative integration (³¹P NMR spectroscopy) against a Ph₃P=O internal standard. ^bRelative to a theoretical maximum of 33%. ^cIsotope equilibration was too rapid for accurate determination of the rate. ^dThe [Na(BARF₂₄)] was doubled. ^eMeasured at -13 °C. ^fAcid was added immediately upon thawing of the reaction solution. ^g1 equiv. of HBARF₂₄ was added.

with the hypothesis that C–O activation alone controls CO₂ reduction chemistry.

We next investigated the kinetics of degenerate CO₂ exchange as a measure for the impact of LA binding on the lability of the Mo–CO₂ interaction (Scheme 3). Exposing solutions of **2**-¹³C and a LA additive to an excess of ¹²CO₂ at 0 °C, resulted in decay of the resonance associated with bound CO₂ in the ¹³C{¹H} NMR spectrum, providing a handle for kinetic analysis. The LA-free exchange rate is over two orders of magnitude faster than those of the LA-stabilized adducts. However, a systematic dependence of the exchange rates on the strength of the added LA was not observed (Table 1). The exchange rates are similar for most of the LAs, irrespective of their AN or the ¹³C chemical shift of the adduct they form.

Scheme 3. CO₂ Self-Exchange in Mo–CO₂ LA Adducts



Some trends are evident from the combined kinetic data (Table 1). Borane LA adducts exchange CO₂ marginally faster in the presence of Et₂O, a competing Lewis base, supporting LA dissociation as a rate affecting step. Likewise, increasing the concentration of LA slows self-exchange, further corroborating a mechanism involving LA dissociation. For the same concentration of LA, the exchange rates are all quite similar and significantly slower than in the absence of LA. The promotion of C–O cleavage in LA adducts correlates with this kinetic factor—the ‘residence time’ of the CO₂ adduct, or the propensity of the substrate to remain coordinated to the metal center—not simply to the degree of CO₂

activation. Further highlighting the importance of kinetic stabilization, C–O cleavage was observed in the absence of LA when protonation was performed at low temperature (Table 1). CO₂ self-exchange likewise showed a significant dampening upon cooling, while the degree of C–O activation does not change. These data suggest that increased residence time of CO₂ at Mo, a consequence of the push-pull interaction, is instrumental for bond cleavage. A competing mechanism for protonation at Mo upon CO₂ dissociation erodes selectivity for CO₂ activation. In terms of augmenting the C–O cleavage preference, increasing the residence time is a decisive factor, independent of the mode of tuning it (temperature vs LA binding).

In summary, a labile Mo(0) CO₂ adduct interacts with a variety of LAs, increasing both the degree of activation and the kinetic stability of bound CO₂. LA addition enhances proton-induced cleavage to CO and H₂O, chemistry that correlates inversely with the kinetics of CO₂ exchange. This work establishes the residence time of a small molecule substrate in the coordination sphere of the metal as a critical factor in engendering desirable transformation chemistry of labile substrates. LAs additives are shown to improve CO₂ cleavage by *kinetic stabilization*, not simply *thermodynamic activation*.

ASSOCIATED CONTENT

Supporting Information

Detailed experimental procedures, full characterization, crystallographic details (CIF), and spectroscopic data. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interests.

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(34) These reactions were performed with strict exclusion of N_2 to avoid potential exchange prior to protonation.

(35) The theoretical maximum of which is 33% (*vide supra*).

(36) Protonation experiments were performed in a 2 PhCl : 1 Et_2O solvent mixture, which solubilizes both alkali metal and borane LAs and their adducts.

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